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(57) Abstract

The present invention provides liquid compositions of matter comprising the insecticide methomyl in a concentrated form that may be readily diluted for spray or other application to crops or foliage. The compositions herein contain methomyl at higher concentrations than those provided by prior art, and methomyl does not crystallize out of the solutions provided at temperatures as low as zero degrees centigrade. Through use of the instant invention, more methomyl may be transported for a given solution volume, and the amount of inerts which are applied to the crops is reduced, thus providing additional advantages from the environmental and cost standpoints.

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Methomyl Solvent Systems

by E. Thomas Marquis and Howard M. Stridde

Cross References to Related Applications

This application claims the benefit of U.S. Provisional Application No. 60/073,988 filed February 6, 1998, which is currently still pending.

Background Information

This invention relates to the preparation and use of solutions containing dissolved insecticidal compounds for which the solubility of the insecticide in the solution is a limiting factor of the concentration at which stable solutions may be stored. More particularly, it relates to the transportation, storage, and use of solutions containing methomyl, using an alkylene carbonate in combination with at least one other oxygen-bearing organic molecule as components of liquid-phase solutions that contain dissolved methomyl.

Methomyl is the methyl ester of N-[(methylcarbamoyl)oxy]thioacetimidic acid. This compound has found widespread use as an insecticide since the early 1970's. Although being a very effective insecticide of relatively low toxicity, the tendency of the material to crystallize out of its solutions at low temperatures is widely known to be a nuisance to personnel involved in the storage, transportation, and use of its solutions. Since it is convenient to provide agriculturally-active compounds dissolved in suitable solvent for later dilution in the field, the tendency of a given material to crystallize out of a concentrated solution is a limiting factor of the effective concentration at which solutions of the material may be prepared for commercial transport and sale. In the case of methomyl, inflated amounts of solution relative to other water-emulsifyable formulations have been found necessary when proceeding according to prior art methods for preparing solutions of methomyl. This has meant that proportionately-inflated amounts of solvent or other inert ingredients must be dispersed along with the active methomyl in a given insecticidal application.

Owing to increasingly stringent controls on permissible solvent releases to the environment by the US EPA and analogous state-level organizations, high levels of solvent release simultaneous to insecticide application are becoming less tolerable. In addition, an inherent part of the costs associated with methomyl transportation are directly attributable to the excess solvent required. There is little doubt that if a new solvent system capable of dissolving larger amounts of methomyl and preventing its low temperature crystallization were available, widespread acceptance by industry would be inevitable. The compositions disclosed herein provide methomyl solutions of higher concentrations over prior art, possessive of a decreased tendency for dissolved methomyl to crystallize out when the solution is subjected to temperatures near zero degrees centigrade for prolonged periods of time.

Summary of the Invention

This invention provides a single-phase, liquid methomyl concentrate composition comprising methomyl and certain organic solvents that can be diluted with water for spray tank use by an end user. A solvent combination according to the invention useful for dissolving methomyl and maintaining it at high concentrations in solution over a wide temperature range comprises a first component that contains at least one alkylene carbonate, and a second component (or co-solvent) that includes least one organic oxygen compound. The alkylene carbonate component may be selected from propylene and butylene carbonate, and the organic oxygen compound may be selected from classes of compounds that may include alcohols, glycols, ketones, ethers, lactones and heterocyclic compounds in which a member of the ring structure contains a keto function, such as N-methyl pyrrolidone.

According to the invention, the combination of alkylene carbonate, methomyl, and other component(s) may contain a high concentration of methomyl, preferably 20 % by weight or more with respect to the total weight of the finished solution, is not chemically

reactive under conditions normally encountered in storage of methomyl solutions, is easily and quickly dilutable with water to the desired spray concentration, and the applied spray does not injure the crops targeted. Additionally, the solution retains a high degree of insecticidal qualities, does not have a tendency to separate into separate liquid layers in storage, and the ingredients possess low hazard potential during and after spray applications as defined by existing local and national environmental regulations.

Description of the Invention

The present invention is directed at solutions comprising methomyl dissolved in a solution combination that comprises a first component containing at least one alkylene carbonate and a second component that includes an organic oxygen compound.

According to this invention, a co-solvent (organic oxygen compound) is combined with an alkylene carbonate, for example propylene carbonate, to provide a solvent combination capable of dissolving high quantities of methomyl, while retarding the tendency of the methomyl to crystallize out of solution at temperatures as low as 0 degrees Centigrade when the methomyl concentration is as high as 30 %. The co-solvent may be selected from various glycols and ethers thereof; ketones; alcohols; lactones; and alkylene carbonates.

To produce a suitable solvent combination according to the invention, one mixes the components of the solvent combination under ambient or slightly elevated temperature, and agitates to produce a homogeneous solution. This typically requires between about 5 minutes and ½ hour of agitation, depending upon the type of vessel in which the mixing is conducted and the agitation employed. (When using laboratory-scale equipment such as a 250 ml beaker and a glass stirring rod, suitable combination is produced within one minute when vigorous stirring with a glass stirring rod is employed). To produce a solution of methomyl in accordance with this invention, one preferably adds the desired amount of methomyl to the solvent combination once the solvent combination

has been made homogeneous, and agitates the solvent until solution is effected. This may be done with or without the assistance of added heat energy, but preferably the solution is heated to about 45 degrees Centigrade prior to the methomyl addition, to facilitate the rapid dissolution thereof.

Several abbreviations are used throughout this specification to denote various chemical species. The key to the abbreviations are:

NMP	N-methyl pyrrolidone
BLO	gamma-butyrolactone
DPNB	dipropylene glycol, mono n-butyl ether
TPM	tripropylene glycol, monomethyl ether
DPM	dipropylene glycol, monomethyl ether
PC	Propylene Carbonate
BC	Butylene Carbonate
CXN	Cyclohexanone
CXL	Cyclohexanol
CX	Cyclohexane

In Table IV abbreviations S2, S3, etc. are used to indicate the first component of the solvent used in making the formulation according to the invention. These designations refer to mixtures containing propylene carbonate ("PC") and butylene carbonate ("BC"), the relative percentages of which compositions are set forth in table I below. Production of the mixtures set forth in Table I consists in simply mixing the materials in a suitable vessel for 10 minutes at ambient temperature. Unless otherwise specified, all percentages in this specification are in parts by weight, based upon the total weight of the finished solution.

Mixture Designation	% PC	% BC
S2	90	10
S3	50	50
S4	10	90
S5	70	30
S6	30	70

Table I – compositions of mixtures designated S2, S3, S4, S5, and S6

By our invention, the compositions of several formulations useful for keeping methomyl in solution at high concentration over a wide range of temperatures have been discovered, the formulations of which are set forth in examples 1 – 12 below. In these examples, synergistic properties of the solvent combinations are believed responsible for their unexpected ability to maintain methomyl in solution in which no crystallization is evident even after prolonged storage at 0 degrees C. The unexpectedness of the success in examples 1 - 12 is evidenced by the compositions of the samples in tables III and IV in which methomyl crystallization was evident after prolonged storage of the solutions at the same low temperatures. The mechanism for the synergy is not currently understood; however, the solvent combinations provided herein are anticipated as being useful for providing stable solutions containing relatively high concentrations of all normally-solid insecticides other than methomyl, including but not limited to derivatives and analogs of methomyl.

Example	PC	BC	TPM	DPNB	CXN	NMP	Methomyl
1	64.8			7.2			28.0
2	64.8				7.2		28.0
3	57.6					14.4	28.0
4	57.6		14.4				28.0
5	58.32	6.48			7.2		28.0
6	32.4	32.4		7.2			28.0
7	32.4	32.4			7.2		28.0
8	19.44	45.36				7.2	28.0
9	19.44	45.36	7.2				28.0
10	6.48	58.2	7.2				28.0
11	56				14.0		30.0
12	18.9	44.1			7.0		30.0

Table II – Successful solution compositions for systems retaining 28.0 and 30 % methomyl dissolved at 0 degrees C with no crystallization evident after one month.

Currently, the most preferred composition is that set forth in example 1. This is most preferred because of the low toxicity of the DPNB, its high flash point, its odorless character, and its relatively low cost.

Compositions for which methomyl crystallization ***was*** evident after 30 days aging at 0 degrees C are set forth in tables III and IV below:

Example No.	PC	BLO	NMP	DPM	TPM	DPNB	CXN	CXL	Methomyl
13	70								30.0
14	63	7.0							30.0
15	63		7.0						30.0
16	63			7.0					30.0
17	63				7.0				30.0
18	63					7.0			30.0
19	63							7.0	30.0
20	56	14.0							30.0
21	56		14.0						30.0
22	56			14.0					30.0
23	56				14.0				30.0
24	56					14.0			30.0
25	56							14.0	30.0

Table III – Failing solution compositions for which methomyl crystallization is evident after storage at 0 degrees C for 30 days.

Example No.	S2	S3	S4	S5	S6	BLO	NMP	DPM	TPM	DPNB	CXL	Methomyl
26	70											30.0
27		70										30.0
28				70								30.0
29					70							30.0
30			70									30.0
31	63					7						30.0
32	63						7					30.0
33	63							7				30.0
34	63								7			30.0
35	63									7		30.0
36	63										7	30.0
37				63		7						30.0
38				63			7					30.0
39				63				7				30.0
40				63					7			30.0
41				63						7		30.0
42				63							7	30.0
43		63				7						30.0
44		63					7					30.0
45		63						7				30.0
46		63							7			30.0
47		63								7		30.0
48		63									7	30.0
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54			63								7	30.0
55					63	7						30.0
56					63		7					30.0
57					63			7				30.0
58					63				7			30.0
59					63					7		30.0
60					63						7	30.0

Table IV – More examples of systems that displayed methomyl crystallizing out when stored at 0 degrees C for 30 days.

The solutions described by the formulae set forth in examples 1 through 12 above are suitable compositions of matter for admixture with water either alone or in combination with various emulsifying agents known to those skilled in the art as being useful for producing final emulsions which may be applied to various crops using spray

or other well-known techniques. These solutions are suitable for use (after appropriate dilution) in the control of pestiferous insects belonging to such orders as Lepidoptera, Homoptera, Hemiptera, Diptera, and Coleoptera, including but not limited to cotton bollworm, tobacco budworm, southern armyworm, soybean looper, beet armyworm, cotton aphid, tarnished plant bug, and white flies. The insects are controlled by applying the solutions to the area to be protected, or to the pests themselves. In the case of agricultural applications, a dispersion or emulsion of the solvents are applied to the foliage to be protected. Effective amounts depend upon the species to be controlled, its life stage, its size and location, the amount of rainfall, time of year, moisture, temperature, type of application and other variables, all of which are known or readily determinable by those of ordinary skill in the art. Generally, dosage levels of between about 0.0625 to 4 kilograms per hectare of methomyl are required, with levels between about 0.125 to 2.0 kilograms per hectare being sufficient in most instances.

The solutions of this invention may be combined with surfactants, wetting agents, dispersing agents, antifoam agents and the like, as such admixtures are typical in the agricultural field and are well-known to methomyl users having ordinary skill. Additionally, the formulations herein set forth may be mixed with fungicides, bacteriocides, acaricides, nematicides, or other biologically active compounds. Suitable surfactants are known to those skilled in the art, and include without limitation sodium lauryl sulfate and its functional anionic, non-ionic and cationic equivalents, as such are well-known to artisans of ordinary skill.

As used in this specification and the appended claims, the term "concentration of methomyl" relates to the amount of methomyl that is dissloved in either a neat or a mixed liquid solvent combination. Methomyl is known to be soluble in various organic solvents to varying degrees; however, most solvents in which it has appreciable solubility are not approved for spray use on crops or foliage. Of those solvents that are acceptable for

spray use, the solubility of methomyl therein is not as high as is desired, and is typically on the order of only about 20 % by weight. As used in this specification and the appended claims, the term "high concentrations of methomyl" means a concentration of methomyl in solution of at least 20 % by weight based upon the total weight of the solution. According to this invention, stable solutions having methomyl concentrations as high as 30 % may be prepared, which permits one-and-a-half times as much active chemical to be transported per given volume over prior art solutions containing only 20% methomyl.

As used throughout this specification and the appended claims, the term "organic oxygen compound" means a chemical compound whose molecular structure includes carbon atoms and oxygen atoms, including compounds belonging to the classes: alcohols, ethers, glycols, polyalkylene glycols, ethers of glycols, ethers of polyalkylene glycols, ketones, pyrrolidones, and lactones, including substituted analogs or derivatives of compounds within these classes, whether the substituents are straight chain, branched, aromatic, or aliphatic. Although specific members of these classes of compounds are illustrated herein as being employable for achievement of the results desired with respect to the spirit of this invention, other members of each class of these compounds are useful as functional equivalents in such regard, when employed at effective amounts readily determinable by an artisan of ordinary skill without undue experimentation, in accordance with the teachings herein.

A typical means by which the instant invention may be employed in the destruction of unwanted pests is by diluting a composition of any one of examples 1 through 12 with a desired amount of water, either alone or with additional diluents, which may include but are not limited to dyes, oils, fungicides, bacteriocides, acaricides, nematicides, or fungicides, to produce an emulsion of desired methomyl concentration. The emulsion is sprayed through a conventional atomizer, including as an example

illustrative and not delimitive hereof, a DeVilbiss No. 152 atomizing nozzle available from the DeVilbiss Company, Somerset, Pennsylvania 15501 using atomizing air at 12 p.s.i. onto a cotton, corn, tomato, or other food-bearing plant. Non-food-bearing plants, such as tobacco, may also be the target.

Although this invention has been shown and described with respect to certain preferred embodiments, it is obvious that equivalent alterations and modifications will occur to others skilled in the art upon reading and understanding of this specification and the appended claims. The present invention includes all such modifications and alterations, and is limited only by the scope of the claims which follow.

We Claim:

1) A liquid composition in which high concentrations of methomyl may be maintained in solution over a wide temperature range comprising: methomyl, an alkylene carbonate, and at least one organic oxygen compound.

2) The composition of claim 1 wherein said organic oxygen compound is a polyalkylene glycol.

3) The composition of claim 2 wherein said polyalkylene glycol is a di-, tri-, or tetra-alkyl alkylene glycol.

4) The composition of claim 3 wherein the alkyl portion of said polyalkylene glycol contains between 1 and 12 carbon atoms.

5) The composition of claim 4 wherein said polyalkylene glycol is selected from the group consisiting of: diethylene glycol, triethylene glycol, tertaethylene glycol, dipropylene glycol, tripropylene glycol, and tetrapropylene glycol.

6) The composition of claim 1 wherein said organic oxygen compound is an ether selected from the group consisting of: mono ethers of polyalkylene glycols and di-ethers of polyalkylene glycols.

7) The composition of claim 6 wherein said ether is a mixed ether comprising at least one hydrocarbon chain having between 1 and 12 carbon atoms, either straight chain, branched, or cyclic.

8) The composition of claim 7 wherein said hydrocarbon chain is aliphatic.

9) The composition of claim 1 wherein said organic oxygen compound is selected from the group consisting of: C_1-C_8 alkyl ethers of a polyalkylene glycol, C_1-C_8 aryl ethers of a polyalkylene glycol.

10) The composition of claim 9 wherein said ether is selected from the group consisting of: C_1-C_4 ethers of dipropylene glycol, and C_1-C_4 ethers of tripropylene glycol.

11) The composition of claim 1 wherein said organic oxygen compound comprises a ketone function.

12) The composition of claim 1 wherein said organic oxygen compound is selected from the group consisting of: N-methyl pyrrolidone, gamma-butyro lactone, cyclohexanol, cyclohexane, and cyclohexanone.

13) The composition of claim 1 wherein said temperature range is from about 0 degrees Centigrade to 20 degrees centigrade.

14) The composition of any of claims 1 through 13 in which the concentration of methomyl is greater than about 25 % by weight based upon the total solution weight.

15) The composition of claim 1 wherein said alkylene carbonate contains between about 2 and 6 carbon atoms per molecule.

16) The composition of claim 15 wherein said alkylene carbonate includes at least one carbonate selected from the group consisting of: ethylene carbonate, propylene carbonate, and butylene carbonate.

17) The system according to claim 16 containing at least one organic oxygen compound selected from the group consisting of: polyalkylene glycols, monoethers of polyalkylene glycols, diethers of polyalkylene glycols, ketones, lactones, pyrollidones, and alcohols.

18) A liquid composition of matter comprising:

a) at least 24 % methomyl;

b) at least one alkylene carbonate; and

c) a third chemical species selected from the group consisting of polyalkylene glycols, ethers of polyalkylene glycols, ethers, lactones, alcohols, ketones, and heterocyclic compounds comprising a ketone function,

in which the alkylene carbonate and the third chemical species are present in amounts effective for maintaining all methomyl present in solution at any temperature in the range of between 0 degrees and 20 degrees centigrade.

19) A composition as in claim 18 wherein the total amount of alkylene carbonate present independently comprises any amount between 19.0 % and 65.0 % of the total solution composition by weight.

20) A solution according to claim 18 wherein said at least one alkylene carbonate comprises a mixture of propylene carbonate and butylene carbonate in which the ratio of propylene carbonate to butylene carbonate is in the range of 10:1 to 1:10.

21) A solution according to claim 18 wherein said ratio is between 1:3 to 3:1.

22) A solution as in claim 18 wherein said third chemical species is independently present in any amount between 5.0 % and 15% of the total solution by weight.

23) A composition according to claim 18 wherein methomyl is present in an amount of at least 28 %.

24) A composition according to claim 18 wherein methomyl is present in an amount of at least 30%.

25) The process of killing insects that comprises the steps of: a) providing a composition according to claim 17; b) adding to said composition at least one material selected from the group consisting of: water, a dye, an oil, a fungicide, a bacteriocide, an acaricide, a nematicide, or a fungicide; and c) contacting the resulting material onto crops or foliage.

26) A process according to claim 25 wherein said oil is an ester of glycerine in which at least one of the acid functions contains between about 8 and 24 carbon atoms.

INTERNATIONAL SEARCH REPORT

Inter. .onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A01N47/24 //(A01N47/24,43:36,43:08,35:06,31:06,31:02,25:02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU 592 970 B (SHELL CHEMICAL AUSTRALIA PROPR) 1 February 1990 see page 2, paragraph 1 see page 3, paragraph 2 see page 5, paragraph 3 - page 15, paragraph 3	1-26
A	AU 568 717 B (SHELL CHEMICAL AUSTRALIA PTY L) 7 January 1988 see page 2, paragraph 1 see page 3, paragraph 4 - paragraph 5 see page 5, paragraph 1 - page 11, paragraph 1	1-26
A	EP 0 189 588 A (HOFFMANN LA ROCHE) 6 August 1986 see column 1, line 1 - column 2, line 4	1-26

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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7 June 1999	18/06/1999

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INTERNATIONAL SEARCH REPORT

Inter. onal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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